INTERACTION OF INTERSTITIAL IMPURITIES WITH IRON SUBGROUP METALS IN AS-CAST MOLYBDENUM-BASED DILUTE; SOLID SOLUTIONS

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INTERACTION OF INTERSTITIAL IMPURITIES WITH IRON SUBGROUP METALS IN AS-CAST MOLYBDENUM-BASED DILUTE SOLID SOLUTIONS

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Several recent studies [1-10] noted the marked decrease in the low-temperature brittleness of chromium, molybdenum, and tungsten ( $Me_{VI}$ ) in the presence of small additions of group VIII metals -- Fe, Co and Ni. Curves with a minimum occurring in the region of dilute solid solutions of  $Me_{VIII}$  in  $Me_{VI}$  are typical for the concentration dependence of the brittle-transition temperature and hardness, from which it follows that certain additions, and at small values, of iron subgroup metals have the most positive effect.

A similar anomalous character of the composition versus property functions (with extrema in the low-addition region) was found in studying the coefficient of thermal expansion and the modulus of elasticity of solid solutions based on MeVI (and other transition metals) [13-16]. The trend of the changes in these properties indicated 1 an increase in the energy of the base-metal crystal lattice in the presence of 0.140.2 atom % of addition, associated with changes in the electronic structure of the matrix when solid substitution solutions are formed [17, 18]. But the effect of trace alloying on mechanical properties was examined from a different viewpoint -- in relation to the possible redistribution of interstitial impurities present in the MeVI [2, 4, 6-12].

It was of interest to compare the mechanical and physical properties of dilute substitution solid solutions based on MeVI

/114\*

<sup>\*</sup> Numbers in the margin indicate pagination in the foreign text.

and defined to what extent the above-mentioned anomalous character of the changes in these properties is associated with change in the structural state -- above all, with change in the solubility of the interstitial impurities. This attempt was made in the present work, dealing with the structure and certain properties of solid solutions of Fe, Co, and Ni in molybdenum.

The selection of the materials for the investigation was determined to a large extent by the fact that the crystal lattice spacing of molybdenum is quite sensitive to the content of solute interstitial impurities, as a result of which it became possible to trace their redistribution between the solid solution and the excess phases, if it occurs in the presence of substitution additions. Small additions of MeVIII lower the brittleness of molybdenum in the as-cast, deformed, and heat-treated states. However, since cold-shortness produces the greatest difficulties in the primary deformation of ingots and welded joints, study of the nature of the positive effect trace alloying has on as-cast alloys is most vital.

Based on studies [19,20], cast molybdenum produced by modern manufacturing methods (with a C content  $\sim 0.01-0.015$ , N and O --  $\sim 0.005-0.003$  weight % each) is a nonequilibrium alloy of the Mo-C system with nonuniform distribution of carbon in both the solid solution as well as in the form of excess inclusions of a carbide phase.

According to theoretical concepts of interstitial solid solutions in metals with BCC [body-centered cubic) structure, the segregation of carbon (and other interstitial impurities) along grain boundaries, subboundaries, dislocations, and other lattice defects [21, 22] and the formation of associations of carbon atoms [23] is predictable. Nonequilibrium crystallization and rapid cooling are added to this concentration inhomogeneity of a hardened solid solution, where both the extent of solution

/115

breakdown as well as characteristics of the distribution of the carbide phase within grains and along their boundaries depend on the cooling rate [24, 25]. The cold-shortness of molybdenum and its analogs are also chiefly associated with the nonuniform distribution of interstitial impurities. The decrease in the low-temperature brittleness in the presence of  $\text{Me}_{\text{VIII}}$  additions is accounted for by the influence of the latter on the distribution and solubility of interstitial impurities [2-12]. From the data in [9, 22, 26-28], the solubility of interstitial impurities in Me<sub>VT</sub> from a Me<sub>VTTT</sub> addition must increase, confirmed by the results of the studies [10, 11] which contain data on the reduction of carbide segregations along grain boundaries. increase in the mobility of disaccations in molybdenum in the presence of 0.1 atom %Fe, Co, and Ni [7, 8] has also been noted, which according to [4] can be a consequence of the breakdown of the solid solution of interstitial impurities. From the data presented we can conclude that trace alloying with iron subgroup metals reduces both intragrain as well as intergrain brittleness, however the mechanism of their favorable effect is far from clear, and the nature of the dependence of the effect on the amount of the addition has not been established.

This present study deals with cast alloys of three binary systems Mo-Fe, Mo-Co, and Mo-Ni in the region of low additions (up to 2 atom [%). The aim of the study included finding the region of substitution addition concentrations having the greatest effect on the mechanical properties of molybdenum, estimating the changes in the solubility of interstitial impurities, in the crystal lattice energy, and in the structure of cast molybdenum caused by trace alloying. Here it proved possible to some extent to find the nature of the interaction of interstitial impurities and substitution additions in the molybdenum matrix.

Ingots of molybdenum and its alloys with iron, cobalt and nickel melted by the noncrucible melt technique in purified helium

were selected for the investigation [29]. The charge materials consisted of metalloceramic molybdenum containing 0.012 weight % carbon (and a several times smaller amount of other interstitial impurities), and iron, cobalt, and nickel of purity 99.9-99.8 weight %.

Mixing of the melt droplets restrained with an electromagnetic field in a suspended state led to the uniform distribution of the alloy addition, and subsequent rapid crystallization of small ingots (13-25 g) in copper chill molds ensured the formation of a fine-grained structure and a significant degree of hardening of interstitial impurities in the solid solution.

A chemical analysis of the ingots was made colorimetrically; quantitative spectral analysis was used to estimate the content of the addition in low-alloy alloys (of the order of 0.1%). The composition of the alloys are given in the table. The content of interstitial impurities in molybdenum and molybdenum-based alloys did not differ appreciably; the amount of carbon (based on combustion data) varied within the limited 0.012-0.015%.

/116

COMPOSITIONS OF BINARY ALLOYS OF MOLYBDENUM WITH Fe, Co, AND Ni BASED ON CHEMICAL ANALYSIS DATA

Alloy num- ber	Fe		Co		Mı	
	at. %	wt. %	at. %	wt. %	at.%	wt. %
1 2 3 4 5 6 7	0.06 0.13 (0.17 0.41 0.65 0.92 1.3)	0,932 0,975 0,1 0,24 0,38 0,54 0,76	0,996 0,163 0,21 0,32 0,45 0,63 1,31	0,053 0,10 0,13 0,21 0,28 0,31 0,83	0,077 0,16 0,3) 0,42 0,96	0,045 0,10 0,18 0,23 0,53 —

A microscopic examination of the alloys showed that in the concentration range studied (0-2 atom (%) the Mo-Fe and Mo-Co alloys are monophase solid solutions, which agrees with literature data on the solubility of Fe and Co in molybdenum [30-32]. The solubility of iron subgroup metals in the alloys decreases in the series Fe \(\to\$ Co \rightarrow Ni; its highest values at elevated temperatures are, respectively, 6.5 and 1 atom %, while it corresponds to a value of \(\times 0.2\) atom % for nickel at 900° [33]. When the microstructure of cast Mo-Ni alloys was inspected, the excess phase -- the compound MoNi [33] -- began to be detectable only in an alloy containing 0.96 atom % Ni (No. 5). With increase in the content of the addition in Mo-MeVIII alloys, a gradual comminution of grains and some development of substructure are detectable.

Mechanical tests and measurements of microhardness were conducted to find the range of optimal concentrations of additions of iron, cobalt, and nickel improving molybdenum plasticity.

Small cylindrical specimens of the alloys (h:d = 2:l = 12 cm: :6 cm) were tested for compression on the universal Instron rupture machine. The compression diagrams for Mo-Co and Mo-Ni alloys are shown in Fig. 1. The spike and plateau of creep typical of metals and alloys with BCC structure containing interstitial impurities can be seen in all the deformation curves. Fig. 2 presents the creep and strength values as functions of alloy composition.

Clearly, a minimum at 0.1-0.2 atom % of cobalt and nickel ( $\sigma_s$  of molybdenum decreases from  $\sim 50~kg/mm^2$  to 36 and 34 kg/mm², respectively) is observed in the concentration dependence of creep, while the strength values increase monotonely. A comparison the composition dependences of  $\sigma_s$  and  $\sigma_b$  on the composition of the Mo-Co and Mo-Ni alloys shows an appreciable rise in the plasticity of cast molybdenum when a certain amount of small substitution addition is dissolved in it.

Microhardness measurements were made to estimate the change in the resistance to deformation of the molybdenum matrix itself, excluding the effect of intergrain boundaries. Considering the microinhomogeneity of the cast structure, use was made of the statistical method of calculating the most probable microhardness of each alloy based on a large number of measurements (60-100 impressions on a specimen were made at a load of 100 and 200 g). The results of measurements for the Mo-Fe, Mo-Co, and Mo-Ni alloys are given in Fig. 2, and by inspecting this figure we see that the hardness minimum lies in the region of addition concentrations for which the greatest plasticity was already noted in compression testing.



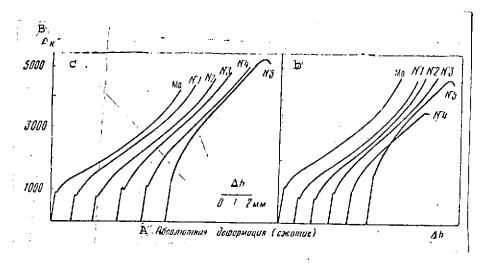


Fig. 1. Compression plot of Mo-Co alloy (a) and Mo-Ni alloy (b).

Key: A. Absolute deformation (compression)

B.  $P_{com}$  [com = compression]

From these data we can conclude that trace alloying with iron subgroup metals improves the plasticity of as-cast polycrystalline molybdenum, and the increase in the plasticity of the molybdenum matrix proves to be substantial. The results of an electron-fractographic investigation of alloys confirmed this. Fig. 3 presents electron-microscopic photographs with intragrain

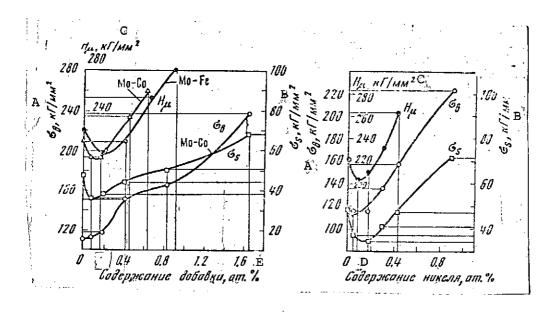


Fig. 2. Dependence of microhardness, creep, and strength on the composition of the alloys Mo-Fe and Mo-Co (a), and Mo-Ni (b).

Key: A.  $\sigma_b$ , kg/mm<sup>2</sup>

B.  $\sigma_s$ , kg/mm<sup>2</sup>

C. kg/mm<sup>2</sup>

D. Nickel content, atom %

E. Content of addition, atom %

fracture of nonalloyed molybdenum (Fig. 3 a) and of its alloy containing 001 atom % Co (Fig. 3 b), for which the lowest creep and microhardness values are characteristic (cf. Figs. 1 and 2). Planar sections of brittle rupture in the fracture of nonalloyed molybdenum can be seen, while only traces of plastic deformation are detectable in the photograph of the alloy.

The composition functions of the mechanical properties of the alloys Mo-MeyIII reveal the region of substitution addition concentrations for which the greatest plasticity is characteristic. An X-ray diffraction pattern study was conducted to find out to what extent the anomalies of mechanical properties observed are associated with changes in the solubility of interstitial/impurities/118 ties. To do this, a precision measurement was made of the crystal lattice spacing of the cast alloys. From the data in the

studies [30-33], addition of 0.1 atom % Fe, Co, and Ni were found to reduce the crystal lattice spacing of molybdenum by an amount smaller than 0.0001 Å, while the same carbon content in a solid solution (0.1 atom %  $^{\circ}$  0.1 weight %) increases the spacing by 0.001 Å [34]. From these data it follows that the changes in the concentration of interstitial impurities in the molybdenum matrix can be recorded as affecting the lattice spacing only if a precision of measurement of the order of  $\pm 0.0001$  Å is insured. The required precision of lattice spacing determination was provided when a reciprocal-diffraction camera with a combination specimen travel feature was used. Its employment provided reflexes of regular form for cast coarse-crystalline alloy specimens.

The second task of the roentgenographic study in this paper was to determine the coefficients of thermal expansion of alloys to estimate changes in the crystal lattice energy of molybdenum when it is alloyed. According to the data in [35, 36], a comparison of the coefficient of thermal expansion of the metal and its dilute solid solutions affords the basis for such an estimate.

In this present work, the coefficients of thermal expansion were calculated as a temperature function of the crystal lattice spacings.

X-ray diffraction patterns at temperature from room temperature to 900°C were obtained in a high-temperature vacuum camera for reciprocal photography [37]. A reflex (321) was used, which

Based on specifications assigned by the Laboratory of Crystallo-chemistry and Roentgenography, accamera with complex specimen travel features (rocking, rotation in combination with horizontal and vertical translation) was designed in the Special Design Bureau of the Institute of Metallurgy imeni A. A. Baykov, USSR Academy of Sciences, by K. V. Bondanrenko, N. V. Shorstkin, and M. V. Marushenko.

in nickel radiation at room temperature is obtained at the angle  $\theta$  of approximately  $80^{\circ}\,.$ 

As the temperature was increased to 900°, the position of the reflex shifted by several degrees, and as a result it was necessary to analyze the effect of various factors (measurement error, physical factors, and photography conditions) on the precision of lattice spacing determination in the range of large reflection angles.

Fig. 4 presents the angular dependence of the error in lattice spacing determination on a number of factors of various kinds. It is clear that sufficient precision — of the order of ±0.0001 Å — is obtained only for relative determinations, with the specimen-film distance kept constant. From an examination of Fig. 4, it also follows that for the photography conditions used<sup>2</sup>, physical and geometrical parameters introduced much smaller corrections than the error of measuring the position of the reflex, on else have an identical effect over the entire range of angles (the correction for refraction); these corrections are also not introduced in relative measurements.

When the lattice spacings were calculated at room temperature and at higher temperatures, consideration was also given to film deformation in photographic processing and shifting of the image in the emulsion layer removed from the specimen. As a result, the relative precision of lattice spacing determination was  $\pm 0.0001$  Å (0.003%), and the error in determining the coefficient

The reflection angle 0 was varied within the limits 77-82°, half of the beam divergence angle  $\alpha$  = 1°, the specimen-film distance R = const (80.5 mm), and the form of the reflex was tedescribed by the relation I = I<sub>0</sub>  $\frac{1}{(1+x^2)^2}$ ; aabs = amea ±  $\Delta$ aD +  $\Delta$ aR +  $\Delta$ ar +  $\Delta$ aL+p+D +  $\Delta$ aV -  $\Delta$ ah; aabs = amea ±  $\Delta$ aD [abs = absolute, mea = measured, v = vertical; h = horizontal, rel = relative]

of thermal expansion  $\Delta\alpha = 2\Delta a/a\Delta t$  was  $\pm 0.05 \cdot 10^{-6}~\text{deg}^{-1}$  ( $\sim 1\%$  of the value being determined).

The data on the measurement of crystal lattice spacings for the alloys Mo-Fe, Mo-Co, and Mo-Ni are shown in Fig. 5. A linear dependence of alloy lattice spacing on composition can be seen; in the region of addition concentrations  $0 \pm 1-0.2$  atom % in which anomalies in mechanical properties are observed, there are no appreciable deviations from additivity. This means that within the limits of the sensitivity to change in the concentration of solute carbon achieved (0.01 atom % % 0.001 weight %), the mean content of interstitial impurities in the solid solution is unchanged.

In contrast ) the coefficient of linear thermal expansion proved to be sensitive to change in the state of the matrix (Fig. 5) -- a well-defined minimum corresponding to the region of anomalous changes in the chemical characteristics can be seen on the isotherms of the composition function of the coefficient of thermal expansion. Evidently, it /must be assumed that alloys containing 0.1-0.2 atom % MeVIII addition, exhibiting greater plasticity and strength than nonalloyed molybdenum, are in a more equilibrium state, compared with it.

The fine structure of molybdenum ingots and its alloys with iron, cobalt, and nickel was studied by diffraction electron microscopy. Cylinders 3 mm in diameter were cut from ingots, and from these cylinders disks 0.5 mm thick were cut with an electric-spark cutter. Hardened layers were removed from both sides of these disks by electrolytic polishing. The final thinning was carried out by the electrolytic jet polishing method on a de- /120 vice described earlier [38]. Specimens prepared in this manner were inspected in an electron microscope with a 200 kV accelerating voltage.

/119

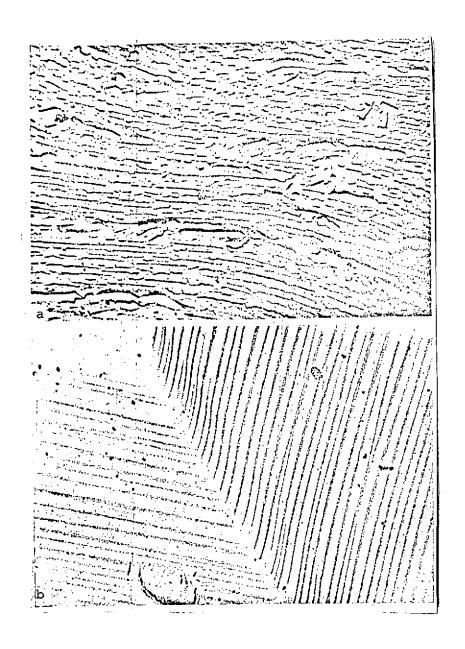


Fig. 3. Photograph of fracture surface of nonalloyed molybdenum (a) and of the alloy Mo-0.1 atom % Co (b).

A noticeable change in fine structure compared with the structure of nonalloyed molybdenum was found in all specimens containing group VIII additions.

Fig. 6 a shows the fine structure of nonalloyed molybdenum. A large number of dispersion inclusions is observed within the grains, forming owing to the homogeneous breakdown of the solid

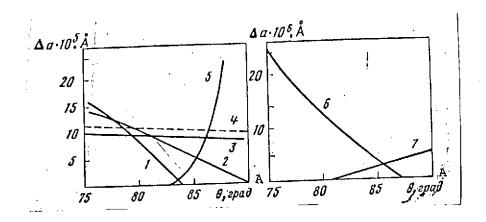


Fig. 4. Precision of the determination of the crystal lattice spacing in the region of high reflection angles as a function of various factors.

- 1)  $\Delta a_R = f(\theta)$  is the error caused by error in measuring the specimen-film distance;
- 2)  $\Delta a_D = f(\theta)$  is the error due to error in measuring the position of the reflex, calculated for  $\Delta \theta = 0.7!$ ;
- 3)  $\Delta a_D = f(\theta)$  -- the same error, but with allowance for the angular dependence of the change in reflex width;
- 4)  $\Delta a_r = f(\theta)$  is the angular dependence of the correction for refraction;
- 5)  $\Delta a_{L+p+D} = f(\theta)$  is the angular dependence of the correction associated with the effect of the Lorentz factor, polarization, and dispersion;
- 6)  $\Delta a_h = f(\theta)$  is the angular dependence of the correction for the horizontal divergence of the beam;
- 7)  $\Delta a_V = f(\theta)$  is the angular dependence of the correction for the vertical divergence of the beam.

Key: A. degrees

solution, and infrequent segregations associated with dislocations can also be seen. Small additions of iron (0.2 atom %) appreciably modified ingot structure: both the dimensions of the segregations as well as their total number were reduced, and the inception of most of them is associated with dislocations (Fig. 6 b).

A further rise in iron content increases the dispersion of segregations at dislocations; dislocations generally free of segregations are observed (Fig. 6 c). It must be noted that large

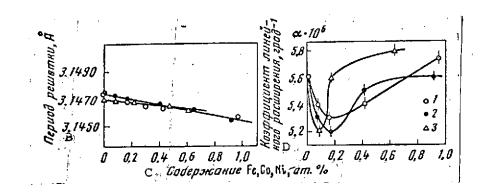


Fig. 5. Dependence of the crystal lattice spacing and the coefficient of thermal expansion on the content of iron, cobalt and nickel in as-cast molybdenum alloys.

Key: B. Lattice spacing

C. Content of Fe, Co, and Ni, atom %

D. Coefficient of linear expansion, degrees 1

rounded inclusion, whose nature cannot yet be established, were detected in several specimens of the alloy Mo + 2 atom % Fe.

Similar changes in fine structure resulting from alloying cast molybdenum were detected upon examining the alloys Mo-Co and Mo-Ni. For example, in the alloy Mo + 0.1 atom % Ni (Fig. 6 d), the dispersion segregations are concentrated along dislocations; with increase in the nickel content, their dispersity rises and dislocations free of segregations appear (Fig. 6 e).

When 0.4 atom % Ni is added, large rounded inclusions appear (Fig. 6 f), whose location indicates their primary origin. They are surrounded by numerous dislocations, which apparently were squeezed out in the matrix as it cooled owing to the difference in the coefficients of thermal expansion of the inclusion and the matrix [39]. It can be assumed that there are intermetallic inclusions, since the solubility of nickel in molybdenum is slight (of the order of ~l atom %) [33], and significant fluctuations in the solid-solution composition are possible resulting from nonequilibrium crystallization.

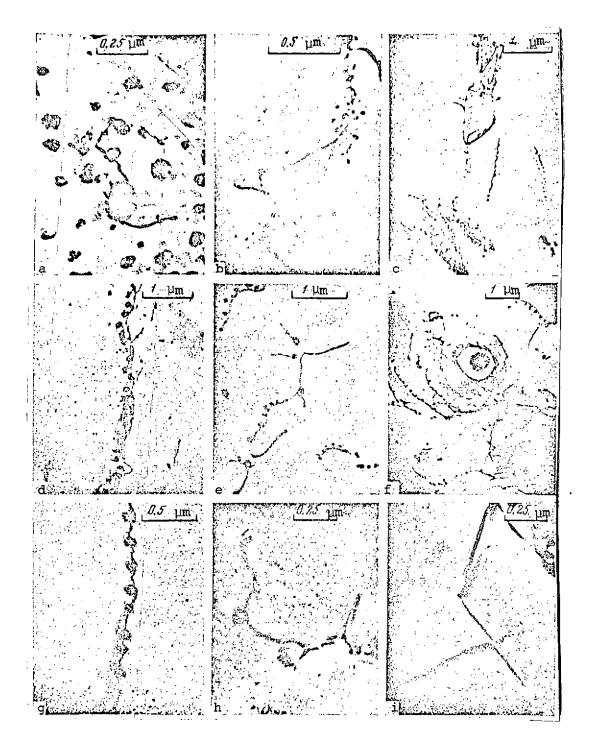


Fig. 6. Electron-microscopic photographs of the fine structure of cast alloys Mo-Fe, Mo-Co and Mo-Ni.

The content of the alloying addition, atomic % is as follows: a) as-cast nonalloyed molybdenum; b) 0.2, Fe; c) 2, Fe; d) 0.1, Ni; e) 0.18, Ni; f) 0.4, Ni; g) 0.1, Co; h) 0.16, Co; i) 0.45, Co.

Fig. 6 g, h and i present microphotographs illustrating changes in the fine structure of cast molybdenum when alloyed with cobalt. When 0.1 atom % Co is added, all the segregations are concentrated along dislocations. When the Co content is increased, the number of segregations becomes less, and with further alloying dislocations virtually free of segregations are observed (Fig. 6 i).

Thus, electron-microscopic examination showed that when molybdenum is alloyed with small additions of iron, cobalt, and nickel, the nature of the breakdown of the solid solution of carbon in molybdenum changes. While in nonalloyed as-cast molybdenum, for given rates of hardening and for a given carbon content ( $\sim 0.015\%$  C), the breakdown is predominantly homogeneous, the addition of 0.1-0.2 atom % MeVIII leads to the heterogeneous inception of segregations at dislocations.

Owing to the increase in the solubility in molybdenum in the presence of MeVIII [9-11], supersaturation of the solid solution with carbon decreases in alloys, which initially leads to changes in the nature of the breakdown (for 0.1-0.2 atom % MeVIII addition), and then to its total suppression for large amounts of the addition, as can be seen from the example of the Mo-Co system (Fig. 6, a, g, h, i).

A comparison of the structure and mechanical properties of the alloys Mo-MeVIII showed that the most plastic of these in all three systems are alloys which are characterized by a matrix free of homogeneous segregations and by dislocations immobilized by carbide phase segregations (Fig. 6, b, d, g). As we know [40], in deformation immobilized dislocations serve as sources for the formation of new dislocations, and as a result of the displacement /121 of these in a matrix free of segregations, the progression of plastic deformation is facilitated. With further alloying

(Fig. 6, c, e, h), the number of segregations at dislocations becomes less, and as a result the number of sources of slip dislocations also is reduced. Therefore a further reduction in  $\sigma_{\rm S}$  and  ${\rm H}_{\mu}$  is halted, and at some instant the process of strengthening due to the forming of a complex substitution and interstitial solid solution begins to predominate.

Thus, it is clear that changes in the mechanical properties of the halloys Mo-MevIII are related in some manner with the nature of fine structure changes.

As we can see, the role of iron subgroup metal additions is that, by increasing the solubility of carbon in molybdenum, they modify the phase ratios in the submicrovolumes of the matrix near dislocations, and here it is important to note that the greatest plasticity is not associated with the total disappearance of carbide segregations. Of all the three alloy systems studied (Mo-Fe, Mo-Co, and Mo-Ni), maximum plasticity is noted for alloys with 0.01-0.2 atom % addition, in which the dislocations are immobilized and the matrix is free of carbide particles. This distribution of interstitial impurities proves to be optimal in the sense of the possibility of slip dislocations being producing and their free translation occurring.

The matrix of Mo-Me<sub>VIII</sub> alloys is a complex solid solution --simultaneously both an interstitial and a substitution solid solution; the optimal conditions for its deformation are probably associated with the uniformity of its concentration of grains by volume. Evidently, additions in the amount of 0.1-0.2 atom % also ensures the greatest uniformity of the complex solid solution in an ingot, since the minimum of the composition dependence of the coefficient of thermal expansion that prevails in this same concentration region (Fig. 5) also indicates the highest equilibrium state of the alloy having this composition.

The dependence of matrix properties on changes in fine structure in the submicrovolumes is directly associated with the nonuniform distribution of interstitial impurities in nonalloyed Mo, caused both by the nonequilibrium occurrence of crystallization and cooling, as well as by the selective interaction of these impurities with crystal lattice defects. For the same reason, the substitution additions -- Fe, Co, and Ni will lie near defects and grain boundaries, which was confirmed by several experimental data [41]. Thus, the concentration of both interstitial impurities as well as substitution additions at the sites of the highest interaction (along boundaries and defects) is unknown and can be much higher than their mean concentration. It is therefore difficult to conclude precisely what concentration of substitution addition leads to a specific degree of dissolving of carbides, though adcorrelation between local (along defects) and mean concentration is probable. The analogous concentration dependence of mechanical properties and fine structure changes in all the systems studied indicates this finding.

## Conclusions

- 1. The dissolution of small additions of iron subgroup metals -- Fe, Co, and Ni -- in as-cast molybdenum has the same effect on the mechanical properties of molybdenum -- in a narrow range of addition concentrations, 0.1-0.2 atom %, atrise in the plasticity of the molybdenum matrix is observed, unaccompanied by appreciable change in the mean solubility of interstitial impurities.
- 2. This effect is associated with the redistribution of carbon in local volumes along crystal structure defects and results from the coexistence of a series of factors:
- -- the nonuniform distribution of carbon in cast molybdenum both in the solute as well as the bound state, with its highest concentration along boundaries and defects;

-- the ability of Me<sub>VIII</sub> to increase the solubility of carbon /122 in molybdenum, which at a specific addition concentration leads to optimal conditions of deforming when immobilized dislocations and a matrix free of carbide inclusions are combined in an alloy structure.

Accordingly, it is also clear that when molybdenum undergoes trace alloying, the optimal amount of the Me<sub>VIII</sub> addition is not unchanged, but will depend on the carbon content and the ingot crystallization conditions.

3. Establishing a similar dependence of anomalous change in mechanical ( $\sigma_s$ ,  $H_\mu$ ) and physical (coefficient of thermal expansion) properties of Mo-Me<sub>VIII</sub> alloys on the content of the Me<sub>VIII</sub> addition suggests that the properties of dilute solid solutions of Me<sub>VI</sub> transition metals cannot be regarded within the framework of binary systems. It is highly probably that changes in the physical properties of the base-metal can be associated with the redistribution of the low-solubility interstitial impurities that are present, caused by their interaction with the additions introduced.

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/123

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